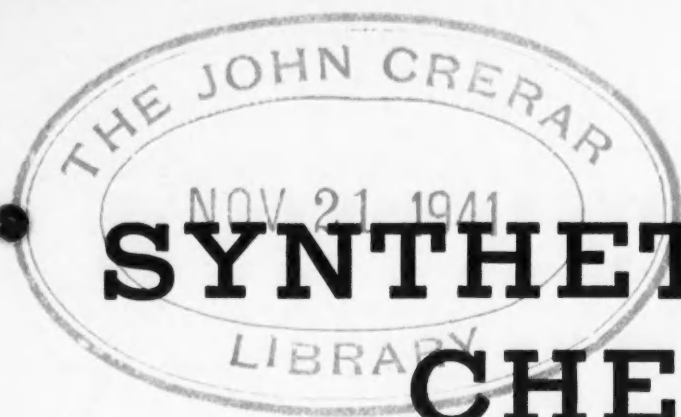


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# SYNTHETIC ORGANIC CHEMICALS

PUBLISHED BY

Eastman Kodak Company, Rochester, N. Y.

VOLUME 13 • 1941 • NUMBER 4

## The Polyene Compounds

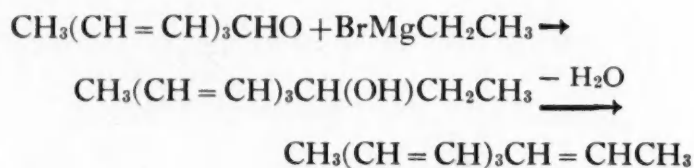
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ALTHOUGH the term *polyene*, which implies many ethylenic double bonds, could logically be applied to aromatic compounds, it is usually reserved for substances that contain open chains, particularly those that have conjugated linkages. Thus, the general formula for the polyene compounds may be written  $R(CH=CH)_nR'$ , in which  $R$  and  $R'$  are radicals and  $n$  is a positive integer.

In recent years, research on the synthesis of the polyenes has been especially associated with the name of Richard Kuhn, and he and his co-workers have succeeded in preparing compounds in which the conjugated chain is extremely long, such as  $C_6H_5(CH=CH)_{15}C_6H_5$ .

The simplest aliphatic series of polyenes is, perhaps,  $CH_3(CH=CH)_nCH_3$ , the higher members of which may be prepared as follows—

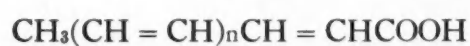
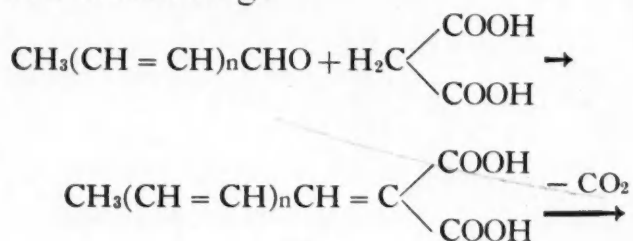


The final step, dehydration, is effected by the use of a 1% ethereal solution of p-toluenesulfonic acid. The hydrocarbon  $CH_3(CH=CH)_6CH_3$  was obtained in this manner, starting with  $CH_3(CH=CH)_3CHO$ , and it was the first colored, purely aliphatic hydrocarbon to be produced; it crystallizes in the form of lemon-yellow

needles having a melting point of  $205^\circ$ .

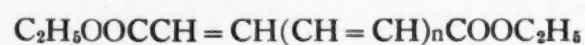
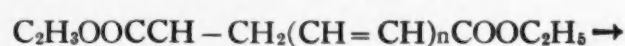
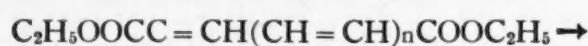
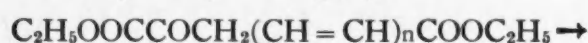
Members of the series  $CH_3(CH=CH)_nCHO$  that are necessary for these syntheses are prepared by condensing acetaldehyde with crotonaldehyde, in the presence of piperidine (1); or by condensing crotonaldehyde with itself, in the presence of piperidine acetate (2). Complex mixtures are usually obtained, and they are separated by fractionation. The aldehyde  $CH_3(CH=CH)_5CHO$  is made by the second method given.

The corresponding series of acids,  $CH_3(CH=CH)_nCOOH$ , are prepared by condensing the polyene aldehydes with malonic acid, in the presence of pyridine (piperidine is also required in the case of the higher vinylene homologs), followed by the elimination of  $CO_2$ ; the liberation of  $CO_2$  is spontaneous in the lower homologs—

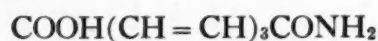


These homologs of crotonic acid are used in the preparation of the dicarboxylic acid series  $COOH(CH=CH)_nCOOH$ . The crotonic acid homolog is esterified and the ester thus formed is condensed

with ethyl oxalate, using potassium ethoxide or pyridine as a catalyst. The compound obtained is acetylated and reduced by aluminum amalgam, and the elements of acetic acid are removed by caustic alkali; in the final step the diester is hydrolyzed (3, 4) —

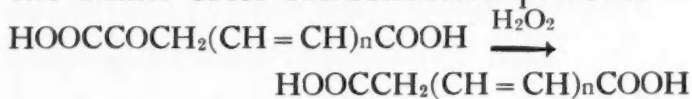


This series of reactions produces dicarboxylic acids that contain one more vinylene group than the original crotonic acid homolog, but dicarboxylic acids that contain the same number of vinylene groups may be made. Kuhn, Köhler, and Köhler (5) showed that the amide of an acid,  $\text{CH}_3(\text{CH}=\text{CH})_n\text{COOH}$ , is oxidized when fed to rabbits, the half-amide of hexatriene dicarboxylic acid, for example, being obtained from the rabbits' urine in a yield of 42% —



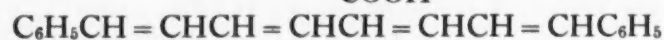
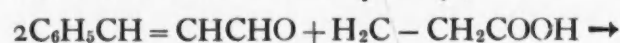
The free acid is readily procurable from the amide, by hydrolysis.

A number of dicarboxylic acids,  $\text{HOOCCH}_2(\text{CH}=\text{CH})_n\text{COOH}$ , are also known. A general method for their preparation (6) is to oxidize, with hydrogen peroxide, the acid that corresponds to the oxalic ester condensation product —



In the aromatic series the diphenyl polyenes,  $\text{C}_6\text{H}_5(\text{CH}=\text{CH})_n\text{C}_6\text{H}_5$ , have been extensively investigated, and a number of methods are available for their synthesis. Cinnamaldehyde may be con-

densed with succinic acid, by the use of lead oxide as a catalyst (7) —



Similarly, the use of  $\text{C}_6\text{H}_5(\text{CH}=\text{CH})_2\text{CHO}$  in place of cinnamaldehyde gives  $\text{C}_6\text{H}_5(\text{CH}=\text{CH})_6\text{C}_6\text{H}_5$ . The higher vinylene homologs of succinic acid —  $\text{HOOCCH}_2(\text{CH}=\text{CH})_n\text{CH}_2\text{COOH}$ , where  $n$  is 1 or 2 — may also be used (3). Certain higher vinylene homologs of cinnamaldehyde are obtainable by condensing it with crotonaldehyde, in the presence of piperidine acetate (8) —

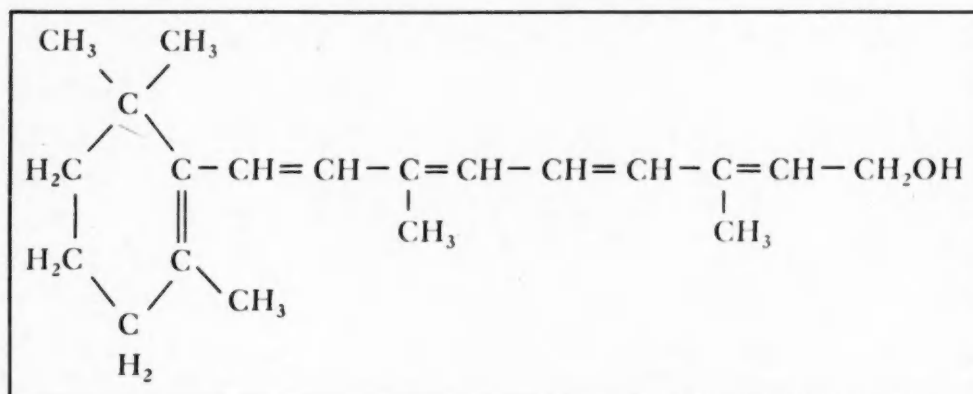
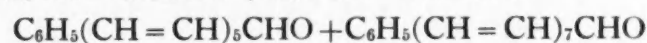
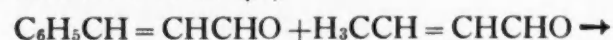
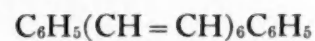
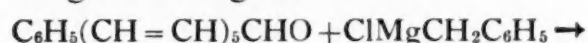
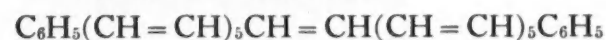
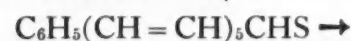
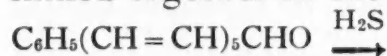


FIGURE I — Structural formula of vitamin A.

These higher aldehydes form diphenyl polyenes, when treated with a benzyl Grignard reagent —



A method that has been successfully used in preparing extremely long chains consists of converting a long-chain aldehyde into the corresponding thio- or seleno-aldehyde, by the action of  $\text{H}_2\text{S}$  or  $\text{H}_2\text{Se}$ . The sulfur or selenium is then removed with piperidine, or a similar amine, or with a metal or metal carbonate. The unsaturated residues become linked together in the process (9) —



The resulting hydrocarbon was obtained



as an extremely insoluble, high-melting, violet-black solid, and by starting with the aldehyde  $\text{C}_6\text{H}_5(\text{CH}=\text{CH})_7\text{CHO}$ , it was

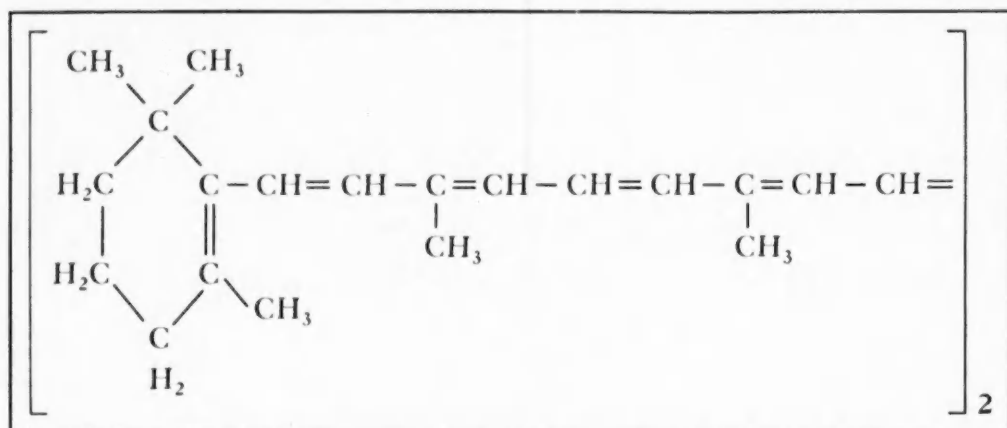


FIGURE 2—Structural formula of  $\beta$ -carotene.

found possible to prepare  $\text{C}_6\text{H}_5(\text{CH}=\text{CH})_{15}\text{C}_6\text{H}_5$ , which was excessively insoluble and still more deeply colored.

Certain polyene compounds are of considerable biological significance. Vitamin A is a primary alcohol containing a long conjugated chain and has the structure shown in Figure 1. This vitamin is closely related to  $\beta$ -carotene, which is represented in Figure 2.

The polyene compounds are characterized by well-defined absorption spectra, and these shift toward the longer-wave-length region of the spectrum as the length of the chain increases. The amount of this vinylene shift varies from series to series, but is usually less than 400 Å. and tends to decrease as the series is ascended. In the typical series of the diphenyl polyenes,  $\text{C}_6\text{H}_5(\text{CH}=\text{CH})_n\text{C}_6\text{H}_5$ , the increase from  $n=1$  to  $n=2$  causes a shift of 330 Å. for the principal band, when the absorptions are determined in benzene. Succeeding shifts are 250, 270, 200, 210, and 200 Å., so that although the decrease in the shift is not regular, nevertheless, the latter three differences are less than the former three. The first few members of this series absorb entirely in the ultraviolet and the bands gradually move further

into the visible region. In a series such as this, where the vinylene shifts are not great and tend to decrease, absorption in the longer-wave-length regions of the spectrum, producing deep colors, such as blue, is extremely difficult to attain, even with long conjugated chains.

From the spectroscopic standpoint, it is interesting to compare the polyene compounds with

the polymethine dyes, such as the typical cyanine series illustrated in Figure 3. In this series the lowest member,  $n=0$ , is already yellow and an addition of vinylene groups produces shifts that average about 1000 Å., and which are, therefore, much greater than those in the diphenyl polyene series. Furthermore, these large shifts show no sign of diminishing as the series is ascended and, thus, absorption in the longer-wave-length regions of the spectrum, giving rise to deep colors, such as blue and green, is quite com-

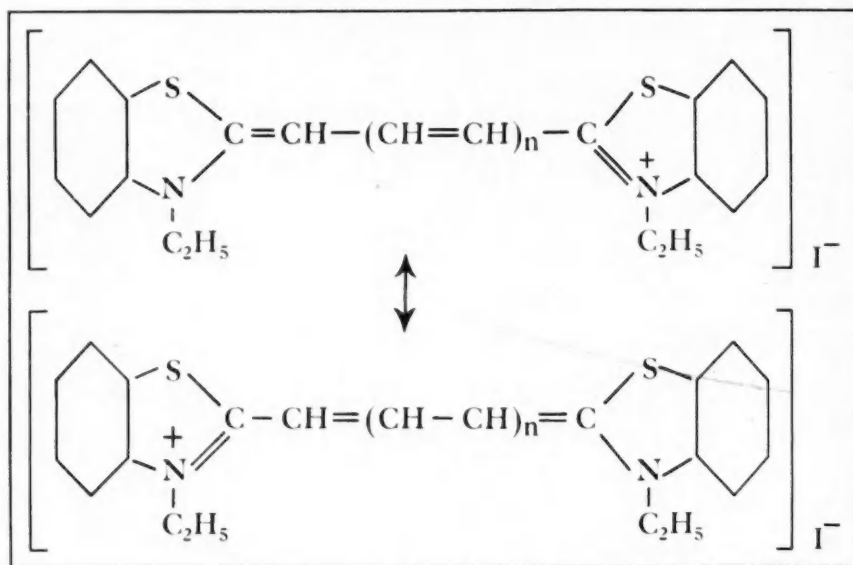
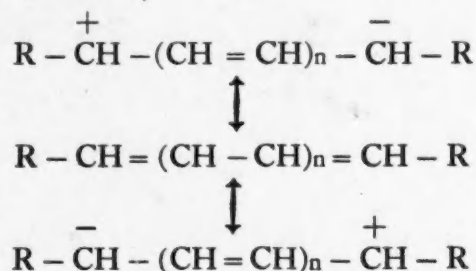


FIGURE 3—Structure of cyanine dye series.

monly encountered in the cyanine dyes.

This marked difference in absorption between the two classes of compounds may be explained on the basis of the resonance theory. In the symmetrical cyanines the dye may be defined by two

identical extreme resonance configurations, as shown in Figure 3, there being complete degeneracy of these resonating structures, whereas this is not the case with the polyenes. Resonance structures, such as the dipolar forms (first and last below)—



may be devised, but their energy is much higher than that of the structure repre-

sented by the "classical" formula, and the degeneracy of the configurations is, therefore, restricted.

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- (5) Hoppe-Seyler's *Z. physiol. Chemie*, 247, 197 (1937).
- (6) Grundmann, *Ber.*, 70, 1148 (1937).
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- (9) Idem, *Angew. Chem.*, 50, 707 (1937).

## A Laboratory Extraction Apparatus

THIS APPARATUS is designed for the extraction of solids by means of volatile liquids, in such cases where the quantities are too large for the ordinary Soxhlet extractor. Its chief advantage is that it may readily be assembled from the usual laboratory glassware.

The flasks may be of any size convenient for the amount of material to be extracted. The illustration shows a 22-l. flask for containing the solid, and a 5-l. flask for boiling the solvent and collecting the extract. The thistle tube filter head is about 40 mm. in diameter, but in any case it should be as large as the neck of the flask will permit. When low-boiling solvents are used, the rate of extraction is usually limited by the capacity of the condenser. For this reason, and also to prevent the loss of liquid, the condensing system should be as large and as efficient as possible.

The filter on the tube in the larger flask is simply a piece of cloth or paper tied over the end of the thistle tube; this permits the use of a variety of filter media such as paper of different degrees of porosity, cotton, or woolen or glass cloth. When employing solvents that affect the stoppers and tubing, these parts should be wired in place.

In normal operation, the extraction flask is half-full of solvent and material

to be extracted. The pressure available for filtration is the liquid head above the open end of the inlet tube. An advantage of the inverted filter surface is that there is less tendency for the solids, especially fines, to pack on the filter and retard passage of the liquid.

A slight modification of the design—a decrease in the size of the return tube and an increase in the size of the distilling flask—provides an intermittent flow like that of a Soxhlet extractor.

